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H2O Outgassing from Silicones

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Disclaimer

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ABSTRACT

In this fiscal year, we have tested the H_2O outgassing model for TR55 against independent core tests performed at different temperatures by our collaborators at Y12 [1]. At higher temperature (~ 71^{o}C), the model properly predicts moisture outgassing from TR55 over the entire experiment. At lower temperature (~ 42.5^{o}C), the model correctly predicts long-term moisture outgassing. However, in short-term limit, a better fit with core tests might be expected when the diffusion effect of H_2O through the silicone matrix is included into the model in the near future. A lookup table for the moisture content as well as moisture outgassing kinetics for M9787 which have previously been heated to 460K for one day and then exposed to relevant low levels of moisture is also now available as a reference for engineers/technicians in the fields.

EXPERIMENTAL METHODS and ANALYSIS TECHNIQUES

Our experimental investigation involved a combination of temperature programmed desorption (TPD) experiments, isothermal desorption experiments and isoconversion technique. The details of the experimental methods and analysis techniques can be found in reference [2].

The lookup table for M9787 involved isothermal heating of M9787 samples in an ultrahigh vacuum (UHV) chamber at 187^{o}C for 24 hours. The samples were then cooled down to room temperature and transferred into a load-lock where the samples were exposed to low levels of moisture for pre-determined amounts of time. At the end of the moisture exposure, the samples were transferred back into the main UHV chamber where TPD were performed to determine the moisture contents and kinetics of the samples.

RESULTS & DISCUSSION

Comparing TR55 outgassing model with core tests:

In Fig. 1, the black curve represents the amount of gas generated from 18.9 grams of TR55 at 75.7 ^{o}C by our collaborators at Y12 [1]. The blue curve represents the gas generation from the same moisture source as predicted from the kinetics obtained by TPD [2,3]. The red band in Fig. 1 represents a ± 35 % error bar associated with our prediction modeling for this moisture source. Fig. 2 represents a similar comparison between experiment and prediction modeling as at mentioned in Fig. 1 but at 42.5 ^{o}C. It is clear that at lower temperature, our current prediction modeling correctly forecasts the long term outgassing. However, in the short-term limit and at lower temperature, a much poorer fit is seen, probably due to our current ignorance of the diffusion effect of H_2O released from the surfaces of silica fillers through the silicone matrix. We are in the process of measuring this diffusion effect and will include it in our future prediction modeling to improve the accuracy of the model in the short term limit and at lower temperature.

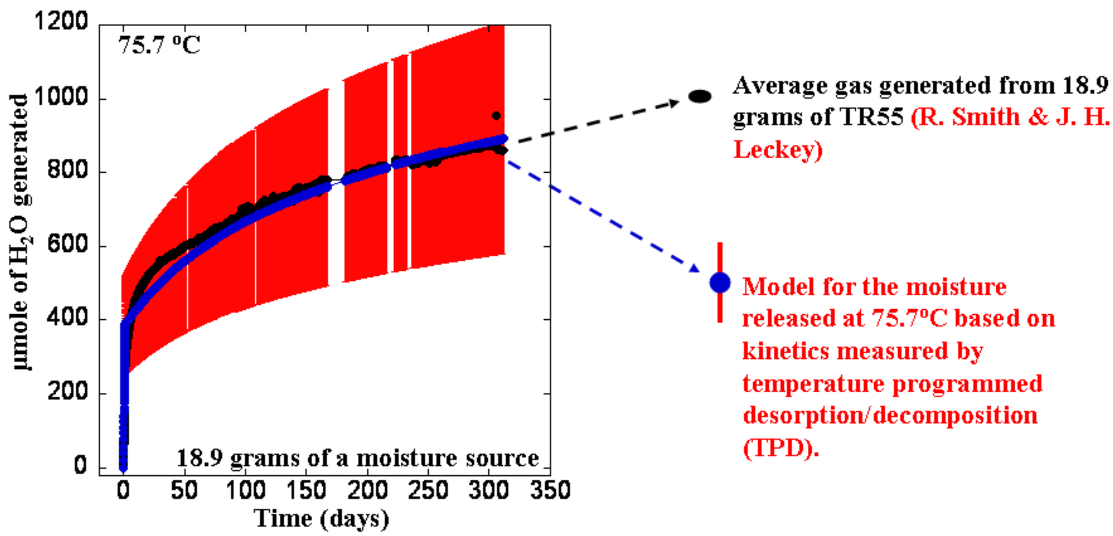


Fig. 1

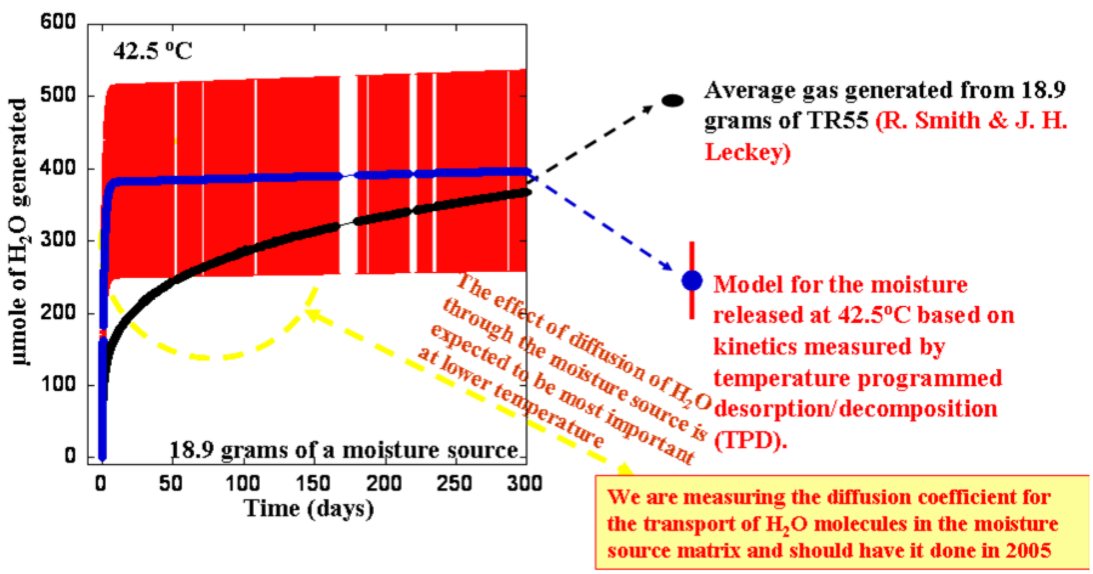
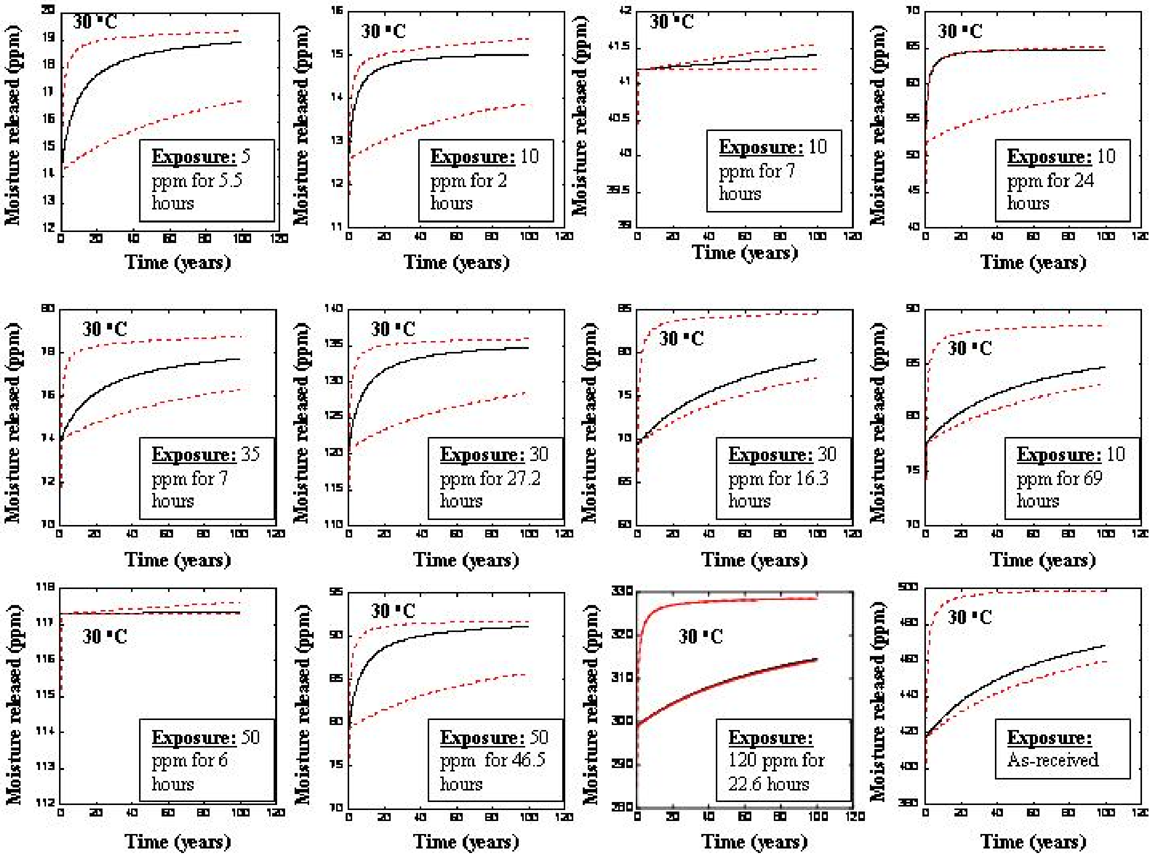


Fig. 2

<u>M9787 moisture outgassing reference lookup:</u>

Below is a reference lookup page for the moisture outgassing from M9787 samples which have been heat-treated and then re-exposed to relevant different low moisture levels. The unit for moisture outgassing in each plot is ppm and represents the amount of moisture expected to be released at 30^{o}C over 100 years in a dry environment. The black line in each plot represents our predictive outgassing modeling for the particular sample under study. The upper and lower red dashed lines in each plot represent the upper and lower limits of our predictive outgassing modeling based on statistics collected on a larger population. The moisture outgassing kinetics as well as the moisture content under each H_2O physisorbed peak (n = 1) and H_2O chemisorbed peak (n = 2) for all samples studied are given in details in APPENDIX A.



M9787-reference lookup page

SUMMARY

We have successfully tested the moisture outgassing model for TR55 against core tests performed independently by our collaborator at Y12. At the presence, our moisture outgassing prediction model has been confirmed to be fairly accurate in predicting long-term moisture outgassing form TR55 at all temperatures. Short-term moisture outgassing prediction at lower temperatures is expected to improve upon future inclusion of the diffusion effect of H_2O in the silicone matrix in to the current model. And finally, a lookup table for the moisture content and outgassing kinetics of M9787 under relevant conditions has been constructed. The accuracy of our current outgassing prediction modeling efforts can still be improved by cross-examining the details of our desorption experiments with other techniques and by including the diffusion effect of H_2O in the silicone matrix in our model.

FUTURE WORK

Besides exploring the diffusion effect of H_2O through the silicone matrix, we also plan to measure the equilibrium vapor pressure of H_2O over the different types of silicones in the coming years. The realism and accuracy of our current moisture outgassing modeling for silicones are expected to improve significantly when the above effects are incorporated into the modeling efforts.

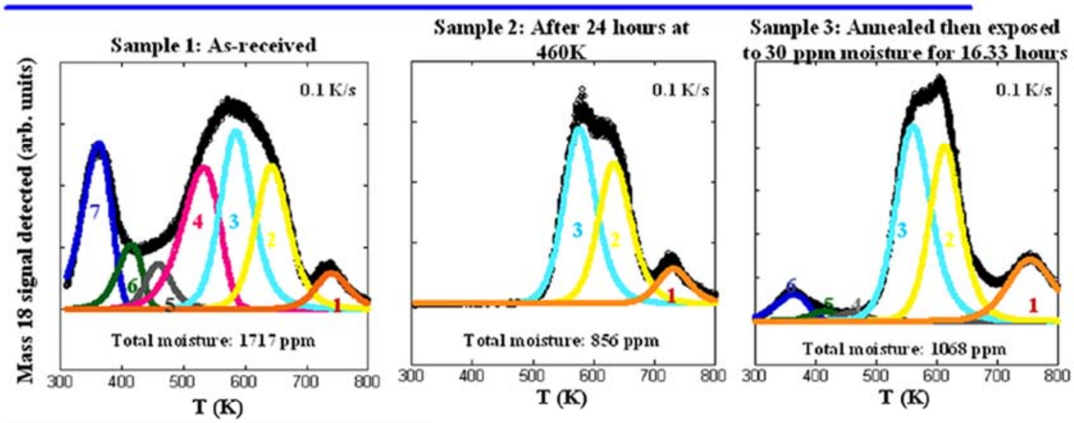
REFERENCES

1. Y12 collaborators: R. Smith, J. H. Leckey, Y12, Oak Ridge.
2. L. N. Dinh, M. A. Schildbach, R. S. Maxwell, W. J. Siekhaus, B. Balazs, and W. McLean II, "H_2O outgassing from silica-filled polysiloxane TR55", J. Colloid Interface Sci. **274**, P. 25-32 (2004).

3. The H_2O desorption peak corresponding to the physisorbed peak with the lowest activation energy barrier (the first peak in the deconvolution of the TR55 TPD spectrum in Ref. [2]) was excluded from contributing to the total outgassing from TR55 represented by the blue curves in Figs. 1 & 2. This is because the moisture under this peak would be completely removed during even a few hours of vacuum pump [2].

APPENDIX A:

M9787 is vacuum dried (at 460 K) but picks up some moisture during the assembly process.



1 (4.7%): n = 2, E = 58.1 kcal/mole, $\upsilon = 1.12 \times 10^{15}\ s^{-1}$
2 (20.1%): n = 2, E = 42.1 kcal/mole, $\upsilon = 1.60 \times 10^{12}\ s^{-1}$
3 (24.5%): n = 2, E = 35.5 kcal/mole, $\upsilon = 1.34 \times 10^{11}\ s^{-1}$
4 (21.6%): n = 2, E = 33.9 kcal/mole, $\upsilon = 3.95 \times 10^{11}\ s^{-1}$
5 (4.8%): n = 2, E = 28.9 kcal/mole, $\upsilon = 3.59 \times 10^{11}\ s^{-1}$
6 (6.3%): n = 1, E = 17.0 kcal/mole, $\upsilon = 4.11 \times 10^{6}\ s^{-1}$
7 (18%): n = 1, E = 10.6 kcal/mole, $\upsilon = 9.44 \times 10^{3}\ s^{-1}$

1 (7.6%): n = 2, E = 57.3 kcal/mole, $\upsilon = 8.41 \times 10^{14}\ s^{-1}$
2 (43.8%): n = 2, E = 41.5 kcal/mole, $\upsilon = 1.21 \times 10^{12}\ s^{-1}$
3 (48.6%): n = 2, E = 34.8 kcal/mole, $\upsilon = 1.01 \times 10^{11}\ s^{-1}$

1 (15%): n = 2, E = 41.1 kcal/mole, $\upsilon = 2.64 \times 10^{9}\ s^{-1}$
2 (34.1%): n = 2, E = 41.6 kcal/mole, $\upsilon = 3.41 \times 10^{12}\ s^{-1}$
3 (43%): n = 2, E = 30.3 kcal/mole, $\upsilon = 2.90 \times 10^{9}\ s^{-1}$
4 (1.4%): n = 2, E = 28.9 kcal/mole, $\upsilon = 3.59 \times 10^{11}\ s^{-1}$
5 (1.5%): n = 1, E = 17.0 kcal/mole, $\upsilon = 4.11 \times 10^{6}\ s^{-1}$
6 (5%): n = 1, E = 9.4 kcal/mole, $\upsilon = 1.27 \times 10^{3}\ s^{-1}$

1 (17.2%): n = 2, E = 44.2 kcal/mole, $\upsilon = 1.19 \times 10^{11}$ s^{-1}

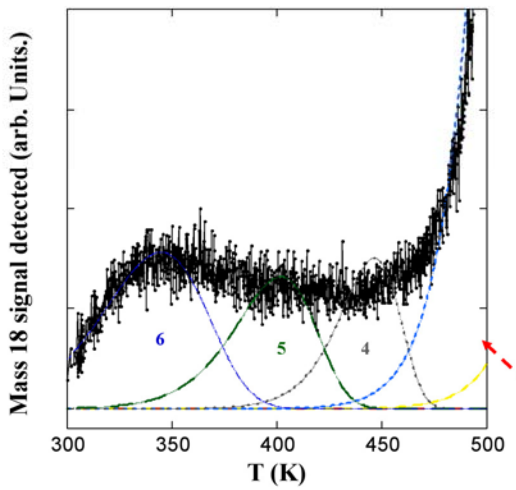
2 (50%): n = 2, E = 36.1 kcal/mole, $\upsilon = 5.06 \times 10^{10}$ s^{-1}

3 (30.7%): n = 2, E = 32.3 kcal/mole, $\upsilon = 3.02 \times 10^{10}$ s^{-1}

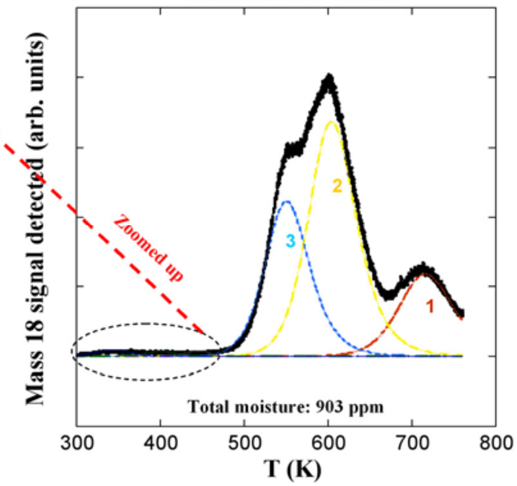
4 (0.55%): n = 2, E = 27.0 kcal/mole, $\upsilon = 1.10 \times 10^{11}$ s^{-1}

5 (0.65%): n = 1, E = 15.9 kcal/mole, $\upsilon = 2.03 \times 10^{6}$ s^{-1}

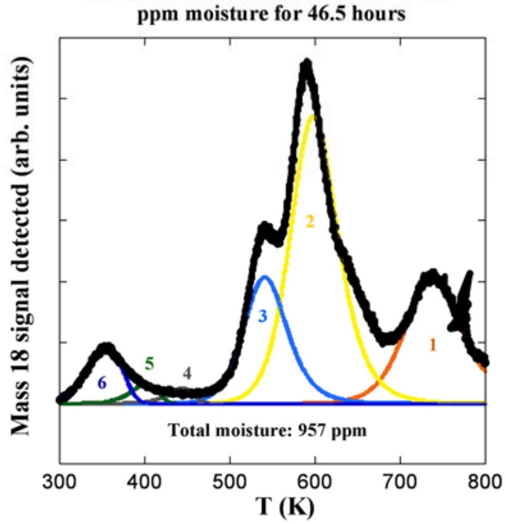
6 (0.92%): n = 1, E = 8.8 kcal/mole, $\upsilon = 1.20 \times 10^{3}$ s^{-1}



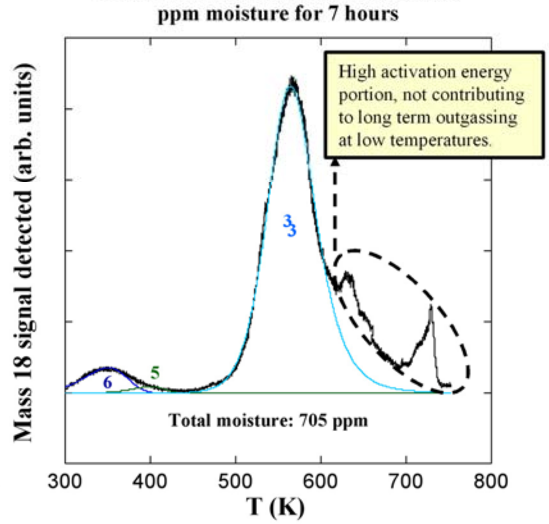
Sample 4: Annealed then exposed to 5 ppm moisture for 5.5 hours



Sample 5: Annealed then exposed to 50 ppm moisture for 46.5 hours



Sample 6: Annealed then exposed to 10 ppm moisture for 7 hours



1 (23.3%): n = 2, E = 45.5 kcal/mole, $\upsilon = 1.06 \times 10^{11}$ s^{-1}

2 (47.8%): n = 2, E = 36.3 kcal/mole, $\upsilon = 8.31 \times 10^{10}$ s^{-1}

3 (19.3%): n = 2, E = 32.3 kcal/mole, $\upsilon = 5.29 \times 10^{10}$ s^{-1}

4 (1.3%): n = 2, E = 26.8 kcal/mole, $\upsilon = 1.01 \times 10^{11}$ s^{-1}

5 (1.8%): n = 1, E = 20.3 kcal/mole, $\upsilon = 6.43 \times 10^{8}$ s^{-1}

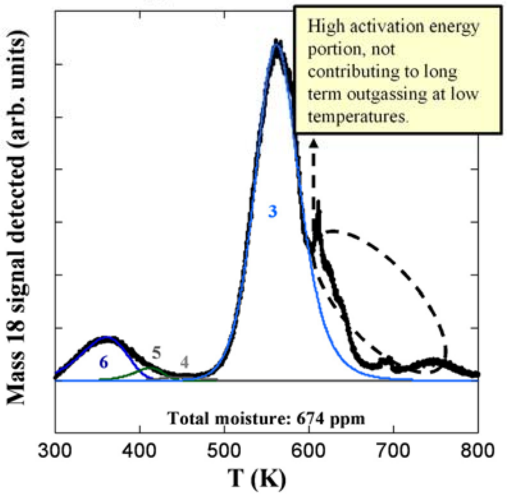
6 (6.5%): n = 1, E = 11.9 kcal/mole, $\upsilon = 8.06 \times 10^{4}$ s^{-1}

3 (75.3%): n = 2, E = 31.5 kcal/mole, $\upsilon = 6.51 \times 10^{9}$ s^{-1}

5 (0.95%): n = 1, E = 17 kcal/mole, $\upsilon = 8.75 \times 10^{6}$ s^{-1}

6 (4.9%): n = 1, E = 9.2 kcal/mole, $\upsilon = 1879.2$ s^{-1}

Sample 7: Annealed then exposed to 35 ppm moisture for 7 hours



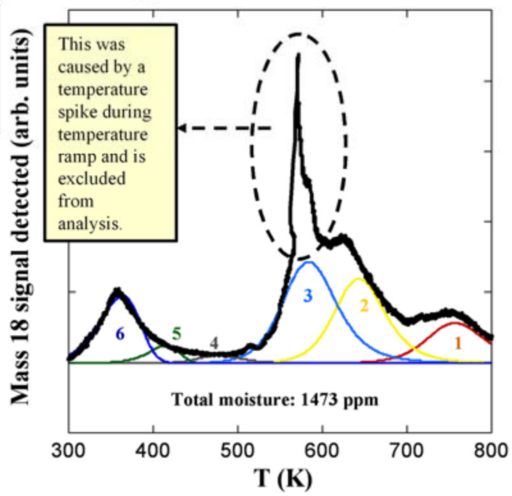
3 (73.9%): n = 2, E = 34.1 kcal/mole, υ = 8.65×10^{10} s^{-1}

4 (0.69%): n = 2, E = 28.5 kcal/mol, υ = 5.32×10^{11} s^{-1}

5 (1.84%): n = 1, E = 18.7 kcal/mole, υ = 3.90×10^{7} s^{-1}

6 (9.14%): n = 1, E = 8.8 kcal/mole, υ = 639.4 s^{-1}

Sample 8: Annealed then exposed to 120 ppm moisture for 22.66 hours



1 (13.0%): n = 2, E = 47.1 kcal/mole, υ = 1.47×10^{11} s^{-1}

2 (28.5%): n = 2, E = 38.2 kcal/mole, υ = 4.03×10^{10} s^{-1}

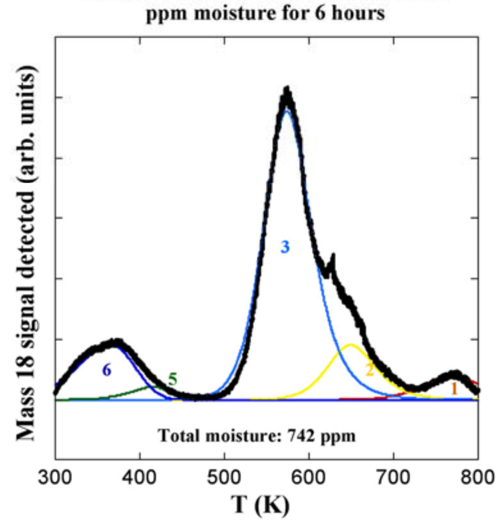
3 (36.2%): n = 2, E = 29.5 kcal/mole, υ = 4.14×10^{8} s^{-1}

4 (2%): n = 2, E = 27.3 kcal/mole, υ = 1.66×10^{10} s^{-1}

5 (3.4%): n = 1, E = 18.6 kcal/mole, υ = 3.05×10^{7} s^{-1}

6 (16.9%): n = 1, E = 9.3 kcal/mole, υ = 1.3×10^{3} s^{-1}

Sample 9: Annealed then exposed to 50 ppm moisture for 6 hours



1 (4.9%): n = 2, E = 46.7 kcal/mole, υ = 6.53×10^{10} s^{-1}

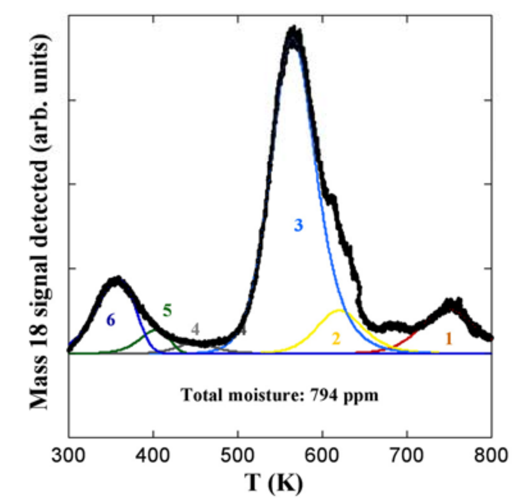
2 (12.7%): n = 2, E = 41.5 kcal/mole, υ = 3.90×10^{11} s^{-1}

3 (66.6%): n = 2, E = 32.6 kcal/mole, υ = 1.17×10^{10} s^{-1}

5 (2.3%): n = 1, E = 14.3 kcal/mole, υ = 1.3×10^{5} s^{-1}

6 (13.5%): n = 1, E = 7.15 kcal/mole, υ = 44.995 s^{-1}

Sample 10: Annealed then exposed to 30 ppm moisture for 27.2 hours



1 (9.9%): n = 2, E = 48.6 kcal/mole, υ = 6.13×10^{11} s^{-1}

2 (9.1%): n = 2, E = 38.8 kcal/mole, υ = 2.19×10^{11} s^{-1}

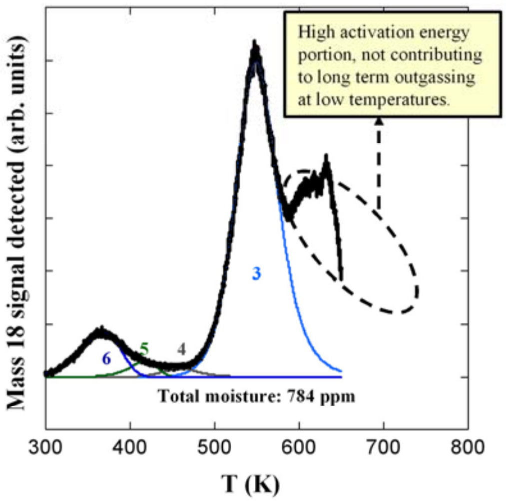
3 (63.9%): n = 2, E = 33.6 kcal/mole, υ = 4.49×10^{10} s^{-1}

4 (1.9%): n = 2, E = 26.0 kcal/mole, υ = 2.37×10^{10} s^{-1}

5 (3.1%): n = 1, E = 18.1 kcal/mole, υ = 2.9×10^{7} s^{-1}

6 (12.1%): n = 1, E = 10.5 kcal/mole, υ = 8.6×10^{3} s^{-1}

Sample 11: Annealed then exposed to 10 ppm moisture for 69 hours



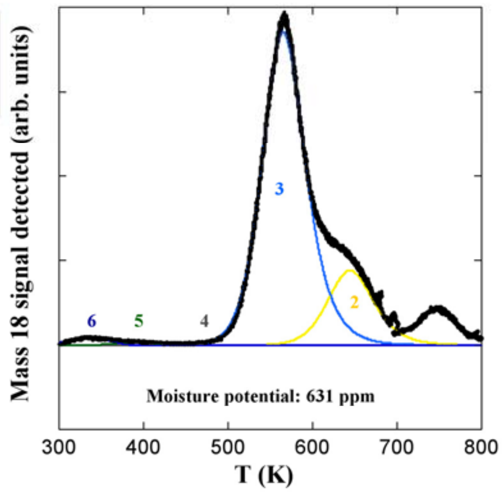
3 (61.6%): n = 2, E = 33.9 kcal/mole, $\upsilon = 1.60 \times 10^{11}\ s^{-1}$

4 (1.4%): n = 2, E = 28.5 kcal/mole, $\upsilon = 2.15 \times 10^{11}\ s^{-1}$

5 (2.0%): n = 1, E = 20.9 kcal/mole, $\upsilon = 4.51 \times 10^{8}\ s^{-1}$

6 (7.9%): n = 1, E = 10.7 kcal/mole, $\upsilon = 7.9 \times 10^{3}\ s^{-1}$

Sample 12: Annealed then exposed to 10 ppm moisture for 2 hours



2 (18.6%): n = 2, E = 43 kcal/mole, $\upsilon = 1.75 \times 10^{12}\ s^{-1}$

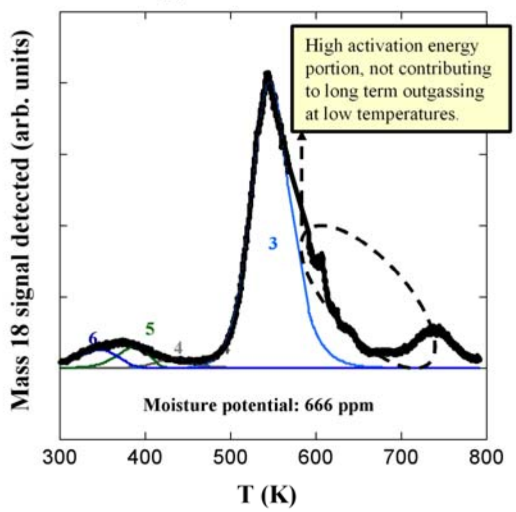
3 (73.3%): n = 2, E = 35.4kcal/mole, $\upsilon = 2.48 \times 10^{11}\ s^{-1}$

4 (0.4%): n = 2, E = 26.3 kcal/mole, $\upsilon = 8.84 \times 10^{10}\ s^{-1}$

5 (0.61%): n = 1, E = 16.5 kcal/mole, $\upsilon = 7.34 \times 10^{6}\ s^{-1}$

6 (1.4%): n = 1, E = 8.8 kcal/mole, $\upsilon = 1.45 \times 10^{3}\ s^{-1}$

Sample 13: Annealed then exposed to 10 ppm moisture for 24 hours



3 (63.97%): n = 2, E = 37.5 kcal/mole, $\upsilon = 5.8 \times 10^{12}\ s^{-1}$

4 (1.95%): n = 2, E = 24.6 kcal/mole, $\upsilon = 1.6 \times 10^{10}\ s^{-1}$

5 (3.82%): n = 1, E = 16.6 kcal/mole, $\upsilon = 6.9 \times 10^{6}\ s^{-1}$

6 (4%): n = 1, E = 9.3 kcal/mole, $\upsilon = 1.8 \times 10^{3}\ s^{-1}$